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(54) Title: JET INK COMPOSITION AND METHOD

(57) Abstract

The present invention relates to an edible ink composition suitable for application through the nozzle of an ink jet printer, which ink comprises an image forming ingredient dissolved or dispersed in a carrier medium, characterised in that the carrier medium comprises acetone. Preferably, the carrier medium comprises the acetone in admixture with water or an alkanol and/or an alkyl ester. The invention also provides a method for printing an image on a substrate using an ink jet printer wherein the ink is an ink composition of the invention.

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## JET INK COMPOSITION AND METHOD

The present invention relates to a composition and to a method for using it, notably to an ink containing acetone as  
5 the solvent or carrier medium and to a method for printing images with the ink compositions using an ink jet printer.

### BACKGROUND TO THE INVENTION:

- 10 A number of forms of ink jet printer have been used to apply ink compositions to a wide range of substrates. In many cases the ink is put up in the form of a solution or suspension in an organic solvent, notably MEK. The use of MEK provides an ink which is highly suitable for use in ink  
15 jet printers, since it gives an ink which can readily be jetted, which is aggressive to many plastic substrates so that the printed image adheres firmly to the substrate, and which dries rapidly so that the printed image resists smudging or smearing allowing the printed substrate to be  
20 handled almost immediately after printing. Furthermore, MEK readily dissolves most of the dyestuffs and other components used in ink compositions, giving the printer the freedom to use a wide range of ink compositions.
- 25 Despite the many technical advantages in the use of MEK, major problems arise in that MEK presents health hazards when inhaled or allowed to contact the skin. Its use is becoming less and less acceptable from an environmental standpoint and it cannot be used to apply coding or other  
30 printing directly to foodstuffs.

It has therefore been proposed to use lower alkanols or water and mixtures thereof as the solvent or carrier medium for inks to be applied to foodstuffs. Whilst such solvent  
35 or carrier media reduce or avoid the physiological problems

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associated with MEK, ink formulations using water as the solvent or carrier dry slowly. In an attempt to reduce the drying time to an acceptable level, typically less than 5 seconds, the water was mixed with alcohol. However, where 5 the level of alcohol was increased beyond 50% by weight, problems were encountered with precipitation of certain commonly used dyestuffs from the composition. Furthermore, the presence of the alcohol caused the printed droplets to spread upon the substrate, giving an unacceptable image.

10

In an attempt to reduce the spreading problem, a number of additives, for example silicones, surfactants and edible oils, were added to the ink composition, without success. Surprisingly, we have found that acetone is particularly 15 suitable for use as the solvent or carrier medium for ink compositions to be applied to foodstuffs and that such a solvent reduces many of the problems associated with water, alcohols and other physiologically acceptable solvents.

20 SUMMARY OF THE INVENTION:

Accordingly, the present invention provides an edible ink composition suitable for application through the nozzle of an ink jet printer, which ink comprises an image forming 25 ingredient dissolved or dispersed in a carrier medium, characterised in that the carrier medium comprises acetone.

The acetone can be the sole solvent or carrier for the image forming component. However, it is preferred to use the 30 acetone in admixture with water or a physiologically acceptable organic solvent, for example a lower alkanol or a lower alkyl ester of a lower alkyl carboxylic acid.

The ink compositions of the invention preferably have a 35 viscosity of less than 40 Cps at 25° C, for example less

than 10 Cps, notably from 1 to 6 Cps, and the desired viscosity can often be achieved by selection of the mixture of solvents used and/or by the addition of a cellulosic or other thickening agent. The thickening agent may also serve

5 as the binder or film-forming agent typically present in ink jet printer ink compositions to provide the printed droplets with a measure of abrasion and/or water resistance.

- Where an alkanol and/or alkyl ester are present, the alkyl
- 10 moieties in the alkanol and ester preferably contain from 1 to 5 carbon atoms, preferably 1 to 3 carbon atoms; and the total number of carbon atoms in both the alkanol and the ester is from 5 to 8.
- 15 The solvent is preferably a mixture of acetone with water, preferably de-ionised or distilled water, in weight proportions of from 9:1 to 1:9, notably from 3:1 to 1:1. Where present, other solvents or carriers are preferably present in less than 30% by weight of the total solvent or
- 20 carrier medium.

The composition of the invention also contains an image forming component which is soluble or dispersed in the solvent/carrier medium. The image forming component can be

25 of any suitable form having regard to the purpose to which the image on the substrate is to be put. Thus, the component can be one which fluoresces under ultra violet light or which can be detected by a magnetic reader. However, it is preferred that the component be one which

30 forms a visible image on the substrate, for example a dyestuff or a pigment. For convenience, the invention will be described hereinafter in terms of a dyestuff.

Preferably, the image forming ingredient is dissolved in the

35 solvent medium and the solvent medium consists predominantly

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of water and acetone. For convenience, the invention will be described hereinafter in terms of a solution of the image forming ingredient in a solvent medium.

- 5 The dyestuff for present use may be put up in an aqueous, ethanol, acetone or other suitable solvent, and the solution incorporated into the solvent medium for present use using any suitable mixing technique. The dyestuff may also be available in the form of a particulate solid or pigment,
- 10 which can be used as such for direct dissolution in the solvent medium. Many forms of suitable dyestuff, notably water soluble food grade dyestuffs, are commercially available and may be used in their commercially available purity. However, some commercial dyestuffs contain
- 15 extenders and residual salts from the neutralisation of sulphonic or other acidic groups in the dyestuff molecule. It is preferred to use dyestuffs which contain less than 5% by weight of these and other materials, excluding the solvent, which may be present.
- 20 It is preferred that the ink composition also contain one or more film-forming resins to aid adhesion of the ink droplet to the substrate and to provide a measure of protection to the dried droplet against abrasion and the action of water
- 25 or other solvents contacting the dried droplet. Typically, such resins will be organic resins as commonly used in ink jet printer ink compositions, and include, for example, acrylic co-polymers, rosin esters, shellac, polyvinyl esters, ketone resins, urea aldehyde resins, vinyl
- 30 chloride/vinyl ether or vinyl acetate co-polymers, cellulose ethers and esters, polyamide resins, styrene/maleate resins, polyvinylpyrrolidone resins, vinyl pyrrolidone/vinyl acetate co-polymers, polystyrene resins, melamine resins, thermosetting acrylic resins, polyurethane resins and
- 35 radiation curable acrylate resins. Such resins can be used

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in their commercially available forms. Where the ink composition is to be applied to a foodstuff, it is preferred to use shellac or a cellulose derivative as the resin.

- 5 It is preferred that the ink compositions for present use contain from 0.1 to 20% by weight of the dyestuff, preferably from 1 to 6%, notably less than 5%; and from 0.05 to 40%, preferably from 0.1 to 20%, by weight of the binder or film-forming component, based on the total weight of the  
10 ink composition.

Where the ink is to be applied through a continuous ink jet printer, it will usually be preferred to use solvent mixtures containing from 3:1 to 1:1 by weight of acetone to  
15 water. It will also usually be necessary to incorporate one or more ionic components into the ink so that it will have sufficient conductivity to accept the charge to be induced in it. Typically, it will be desired to use an ink composition with a conductivity of from 500 to 2500,  
20 preferably 750 to 1250, microSiemens per centimetre. This is achieved by the incorporation of one or more ionic materials into the ink, which may incidentally be present in one or more of the desired components, for example as salts in the dyestuff or the dyestuff itself. Suitable salts  
25 which may be added include edible or food grade ammonium, sodium or potassium salts of organic acids, such as acetic acid, lactic acid or propionic acid, or of inorganic acids, such as hydrochloric, sulphuric or phosphoric acids. The ammoniation of a component of the ink composition may also  
30 be used to provide at least part of the conductivity required in the composition. Such an ammoniated component is often readily soluble in the solvent medium but reverts to a water insoluble form due to loss of the ammonia from the printed droplet, whereby the component provides the  
35 printed droplet with enhanced water resistant properties.

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It is preferred that the component to be ammoniated be a binder, notably an organic resin containing one or more carboxylic acid groups, for example shellac.

5 The ink compositions for present use can be made by any suitable method, for example by mixing together solutions of the components in one or more of the solvents and then diluting the mixture to the desired concentration with further solvent.

10 The invention further provides a process for printing an image with an ink composition of the invention, characterised in that the composition is applied through the nozzle orifice of an ink jet printer.

15 Ink jet printers are non-contact printers in which discrete droplets of the ink are applied to individually selected positions on a substrate so as to form the desired image on the substrate. The ink jet printer can be of the drop on demand type in which discrete droplets of ink are ejected from an array of nozzles past which the substrate passes, the nozzles being activated at the desired frequency and in the desired order to form the desired image on the substrate. Thus, the printer can be one in which ink under 20 pressure flows to the nozzles via valving means which are actuated under the control of a computer or the like to allow ink to flow to the required nozzle to eject a droplet from that nozzle. Alternatively, ink can be fed to an ink chamber provided with a piezoelectric crystal which modifies 25 the shape of the chamber when a voltage is applied to the crystal so as to eject a droplet of ink from a nozzle outlet to the chamber. For convenience such types of printer will 30 be designated generally hereinafter as drop on demand ink jet printers.

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- Alternatively, the droplets can be applied by what is known as a continuous ink jet printer in which ink is fed under pressure from a reservoir through a nozzle to form a jet of ink. This jet is broken up into discrete substantially uniformly sized and spaced apart droplets by applying vibration or pressure pulses to the ink. This can be achieved by vibrating the nozzle or the nozzle assembly by means of a piezoelectric crystal, or by immersing a vibration probe, for example a piezoelectric crystal rod, in the ink itself. The ink is charged by applying a voltage between the ink jet before it breaks up into droplets and a charge electrode, so that each droplet carries a known charge. The charged droplets then pass through a deflection electric field where they are deflected from their straight line of flight by the deflection field applied. The extent of deflection will determine the point at which the droplets strike a substrate passing the printer and the charge and/or deflection fields are varied to direct the droplets to the desired location on the substrate. Droplets which are not to be printed are not deflected but are caught in a catcher or gutter and are returned to the ink reservoir for re-use. Such ink jet printers are generally denoted as continuous ink jet printers hereinafter.
- Many forms of the above types of printer are known and commercially available and may be used without modification in the method of the invention.
- As stated above, the compositions of the invention are especially suitable for use in printing images on foodstuffs or the packaging for foodstuffs since the solvent is edible and indeed forms part of the human metabolic cycle. It is therefore preferred to use components in the composition which are food grade or edible to ensure that the potential benefit of the acetone solvent is achieved.

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The ink compositions of the invention and their application through a commercially available continuous ink jet printer will now be described by way of illustration in the following Examples in which all parts and percentages are 5 given by weight unless stated otherwise:

**Example 1:**

An ink composition was made by mixing acetone (71.1 parts) 10 with de-ionised water (25 parts), adding the dyestuffs Erythrosine E127 (2 parts) and Patent blue V E131 (0.2 parts) and stirring at room temperature (20°C) until all the dyestuff had dissolved. The viscosity of the mixture was adjusted to within the range 3 - 4 Cps at 20°C by the 15 addition with stirring of the hydroxypropyl cellulose sold under the Trade Mark Klucel EF (1.7 parts).

The conductivity of the resultant ink was in the range 1150 to 1250 microSiemens per centimetre. The ink composition 20 could be applied through either a drop on demand printer or through a continuous jet printer to give droplets which dried rapidly and did not spread to an appreciable extent. Substantially all of the acetone in the ink composition evaporated from the printed droplet to give a solid printed 25 droplet which contained edible materials. Since acetone is a material involved in the human metabolic chain, the ink composition can be applied directly to foodstuffs, such as eggs, fruit, pies and pastries as well as to the packaging for these and other foodstuffs.

30

**Example 2:**

The process of Example 1 was repeated, except that the amount of water was reduced to 18 parts and the amount of 35 acetone was increased to 76 parts. The ink could be printed

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as in Example 1, but tended to precipitate the Erythrosine dye upon standing at room temperature for three days, whereas the composition of Example 1 was stable over at least three weeks.

5

Example 3:

An ink composition was made by mixing together acetone (46.8 parts), de-ionised water (21 parts) and ammonia (10% aqueous 10 solution, 4 parts) at room temperature. The dyestuffs Erythrosine E 127 (2 parts) and Patent blue V E131 (0.2 parts) were added to the mixture and stirred to dissolve them. Shellac (50% solution in ethanol) was added and stirred to dissolve it. If solid shellac is used in place 15 of the ethanol solution, dissolution in the acetone/water/ammonia mixture is slow and incomplete unless 10 to 20 parts of ethanol are present in the solvent mixture.

20 The resulting ink can be applied through the nozzle of a continuous jet printer and gives a good print image which is resistant to boiling water for more than 5 minutes. Again, since all the ingredients of the ink are edible or food grade, the printed droplets can be applied directly to 25 foodstuffs.

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CLAIMS:

1. An edible ink composition suitable for application through the nozzle of an ink jet printer, which ink comprises an image forming ingredient dissolved or dispersed in a carrier medium, characterised in that the carrier medium comprises acetone.  
5
2. A composition as claimed in claim 1, characterised in that the acetone is used in admixture with water or a physiologically acceptable organic solvent.  
10
3. A composition as claimed in claim 2, characterised in that the organic solvent is a lower alkanol and/or a lower alkyl ester of a lower alkyl carboxylic acid.  
15
4. A composition as claimed in claim 3, characterised in that the alkyl moieties in the alkanol and/or ester contain from 1 to 5 carbon atoms.  
20
5. A composition as claimed in claim 4, characterised in that the alkyl moieties contain from 1 to 3 carbon atoms; and in that the total number of carbon atoms in both the alkanol and the ester is from 5 to 8.  
25
6. A composition as claimed in claim 2, characterised in that the water is present in from 1:9 to 9:1 parts by weight of the acetone.  
30
7. A composition as claimed in any one of claims 1 to 6, characterised in that it comprises a film forming resin.  
35
8. A method for applying an image forming composition to a substrate using an ink jet printer, characterised in that the composition is one as claimed in any of claims 1 to 7.

**AMENDED CLAIMS**

[received by the International Bureau on 10 August 1992 (10.08.92);  
new claims 9 - 12 added (2pages)]

9. An edible ink composition suitable for application through the nozzle of an ink jet printer to a foodstuff or 5 to packaging in immediate contact with the foodstuff, which ink composition comprises an image forming ingredient dissolved or dispersed in a carrier medium, characterised in that the carrier medium comprises as essential ingredients:
  - A. at least 50% by weight of acetone; and
  - 10 B. at least one other solvent selected from water or a physiologically acceptable lower alkanol and/or a lower alkylester of a lower alkyl carboxylic acid in which the alkyl moieties of the alkanol and the ester contain from 1 to 3 carbon atoms and the total number of carbon atoms in 15 both the ester and the alkanol is from 5 to 8; and in that where water is the other solvent it is present in a weight ratio of from 1:3 to 1:1 of the acetone present, and in that where an alkanol or ester is present it is present in an amount of less than 30% by weight of the total 20 carrier medium.
10. A method for applying an edible image to a foodstuff or to packaging in immediate contact with the foodstuff, characterised in that an edible ink as claimed in claim 9 is 25 applied by an ink jet printer to the foodstuff or packaging.
11. An ink or method as claimed in either of claims 9 or 10, characterised in that the ink composition contains from 0.1 to 5% of an edible dyestuff, from 0.1 to 20% of an 30 edible cellulose ether or ester or shellac as a binder or

film-forming agent to aid adhesion of the ink to the foodstuff or packaging.

12. An ink or method as claimed in any one of claims 9 to 5 11, characterised in that the ink has a conductivity of from 750 to 1250 microSiemens per centimetre and the ink jet printer is a continuous ink jet printer.

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 92/00277

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)<sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C09D11/00

## II. FIELDS SEARCHED

Minimum Documentation Searched<sup>7</sup>

Classification System	Classification Symbols
Int.Cl. 5	C09D

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched<sup>8</sup>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	FR,A,2 339 660 (A. B. DICK COMPANY) 26 August 1977 see page 3, line 7 - line 11 see page 4, paragraph 3 see claims ---	1-4,6-8
X	US,A,4 352 901 (DOROTHY MAXWELL) 5 October 1982 see claims 1,9 ---	1-8
X	FR,A,2 325 704 (AGFA-GEVAERT) 22 April 1977 see claims 1,6; example 1 ---	1,2,6,8
X	GB,A,2 184 742 (CANON KABUSHIKI KAISHA) 1 July 1987 see claims 1-3,5 ----	1,2,6,8
		-/-

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## IV. CERTIFICATION

Date of the Actual Completion of the International Search

20 MAY 1992

Date of Mailing of this International Search Report

10.06.92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

GIRARD Y.A.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	GB,A,2 004 904 (M & T CHEMICALS INC.) 11 April 1979 see page 1, line 28 - line 36 see page 1, line 56 - line 64 see page 1, line 82 - line 83 ----	1-4,7,8

**ANNEX TO THE INTERNATIONAL SEARCH REPORT**  
**ON INTERNATIONAL PATENT APPLICATION NO. GB 9200277**  
**SA 56587**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
FR-A-2339660	26-08-77	US-A-	4070322	24-01-78
		AU-B-	501978	05-07-79
		AU-A-	2157377	03-08-78
		CA-A-	1092268	23-12-80
		DE-A, B, C	2704082	04-08-77
		GB-A-	1543703	04-04-79
		JP-A-	52096106	12-08-77
US-A-4352901	05-10-82	US-A-	4389503	21-06-83
FR-A-2325704	22-04-77	DE-A-	2543092	07-04-77
		BE-A-	846472	23-03-77
		GB-A-	1550851	22-08-79
		JP-A-	52041007	30-03-77
		US-A-	4106027	08-08-78
GB-A-2184742	01-07-87	DE-A, C	3642571	19-06-87
		JP-A-	62283175	09-12-87
		US-A-	4849770	18-07-89
		JP-A-	62260873	13-11-87
GB-A-2004904	11-04-79	AU-A-	3913178	28-02-80
		BE-A-	870535	02-01-79
		DE-A-	2837517	05-04-79
		FR-A-	2404038	20-04-79
		JP-A-	54056505	07-05-79
		NL-A-	7809747	28-03-79
		SE-A-	7809938	27-03-79